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Voltage-dependent conductance states of a single-molecule junction

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Abstract

Ag–Sn-phthalocyanine–Ag junctions are shown to exhibit three conductance states. While the junctions are conductive at low bias, their impedance drastically increases above a critical bias. Two-level fluctuations occur at intermediate bias. These characteristics may be used to protect a nanoscale circuit. Further experiments along with calculations reveal that the self-limiting conductance of the junctions is due to reversible changes of the junction geometry.

(Some figures may appear in colour only in the online journal)

While molecular analogues of many engineering devices exist in nature man-made single-molecule devices are less abundant. One goal of molecular electronics is to employ molecules as functional building blocks in electronic circuits [1–11]. Single molecules connected to two nanoscale electrodes have revealed intriguing properties such as conductance switching, negative differential resistance, and rectification [12]. Passing currents through a molecule inevitably causes heating which may lead to irreversible modification and failure of the molecular junction [13]. We propose a single-molecule junction whose conductance is drastically reduced when a limiting bias voltage is exceeded. As the reduction is reversible, the junction acts as a safety device for protecting nano-systems.

The device is based on voltage-dependent switching of a tin-phthalocyanine molecule (SnPc, figure 1(a)), which is trapped between a Ag(111) surface and the Ag tip of a scanning tunnelling microscope (STM). The current through this Ag–SnPc–Ag contact is large and stable at low positive sample voltage V . At increased voltage the current I fluctuates between two levels, which correspond to tunnelling (low I) or contact (high I). Beyond a limiting voltage (~ 350 mV), the junction remains trapped in the high-impedance tunnelling

state. Once the voltage is lowered below the critical range, the low-impedance contact is re-established. The whole process resembles a sequence of signals indicating three operating conditions, namely on, warning, and off. The mechanism underlying the process is analysed by a series of experiments and nonequilibrium Green's function calculations of the electron transport properties.

The experiments were performed with an STM at 9 K in ultrahigh vacuum. Au(111), Ag(111), and Cu(111) samples and etched W tips were prepared by standard Ar⁺ bombardment and annealing. The tips were dipped into the sample surface to coat them with sample material. Highly purified SnPc molecules were deposited onto the substrates at ambient temperature before transferring the samples to the cold STM. All images were recorded at constant current with voltages applied to the substrates.

Figure 1(b) shows an STM image of two SnPc molecules on Ag(111). The molecules lie flat on the surface maximizing the interaction between their π electrons and the metal. Due to its shuttlecock shape, SnPc is found in two configurations, SnPc-up and SnPc-down, where the central Sn atoms point towards the vacuum or towards the substrate. STM images of the molecule exhibit either a protrusion or a depression [14].

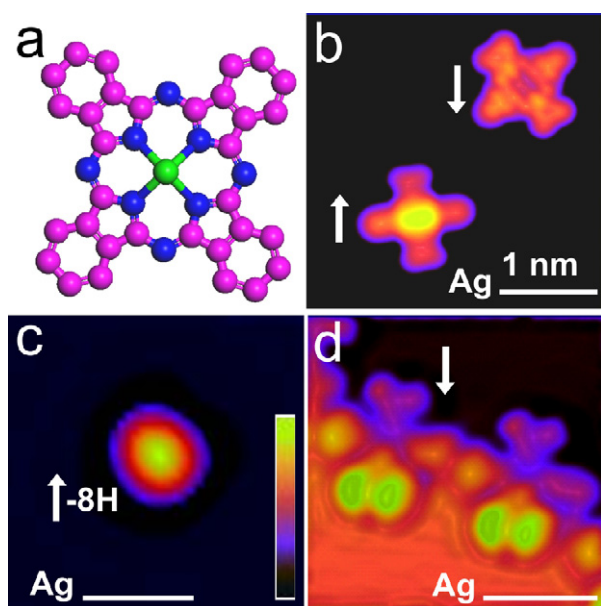


Figure 1. (a) Molecular structure of SnPc (Sn green, N blue, C pink, H not shown). (b)–(d) Constant current STM images of SnPc ($I = 80$ pA). The arrows pointing up and down indicate SnPc with its central Sn ion located on the vacuum and substrate sides, respectively, of the molecular plane. The white scale bars correspond to 1 nm in all images. The bar in (c) shows the false-colour scale used. (b) SnPc on Ag(111) ($V = -50$ mV). (c) SnPc-up on Ag(111) after removing eight peripheral H atoms (-450 mV). (d) SnPc-down at a step on Ag(111) (-450 mV).

To form a molecular junction, the STM tip was centred above a SnPc-up molecule and approached towards the Sn atom [15]. The current through the junction was simultaneously recorded (figure 2(a)). It grows exponentially in the tunnelling region as expected. A sharp increase from ~ 0.06 to ~ 0.78 μA signals the transition to contact. Once contact to the molecule was established, the STM feedback loop was disabled and current–time ($I(t)$) traces were recorded at selected bias voltages. Figure 2(c) shows data for $V = 110$ mV, which is typical of voltages $V < 130$ mV. The current is constant indicating that the geometry of the structure is stable. When V exceeds 130 mV, two-level fluctuations of the current occur. Figure 2(d) was recorded at 200 mV, where I alternates between ~ 0.14 and ~ 1.4 μA . At higher bias, the switching rate initially increases, reaches a maximum at ~ 270 mV and then decreases again. At and above ~ 350 mV, the fluctuations stop and a low and constant current flows (0.2 μA in figure 2(e)). The entire process is reversible. Upon decreasing V , current fluctuations resume and at low bias a large and stable current flows. Figure 3 summarizes the fluctuation characteristics. In the low ($V < 130$ mV) and high-impedance ($V > 350$ mV) states, which correspond to contact and tunnelling, the current is stable. Fluctuations occur at intermediate voltages, where the junction remains in either state over sub-millisecond time intervals.

A number of mechanisms may be invoked to interpret the characteristics described above. (i) The configuration of the SnPc molecule may alternate between its up and down states.

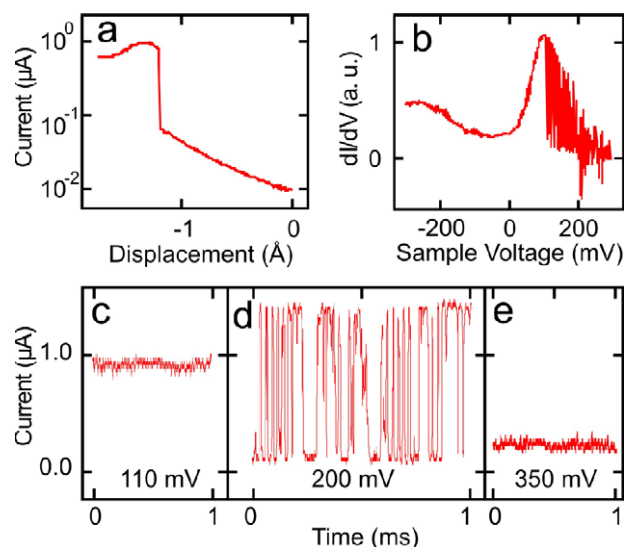


Figure 2. Current through a Ag–SnPc–up–Ag junction. (a) Dependence on the vertical tip displacement at 100 mV. Zero displacement is defined by feedback loop parameters of 100 mV and 10 nA. (b) Spectrum of the differential conductance (dI/dV) of a Ag–SnPc–up–Ag junction at contact. (c)–(e) Time series at $V = 110, 200,$ and 350 mV, respectively, measured at contact with the STM feedback loop disabled.

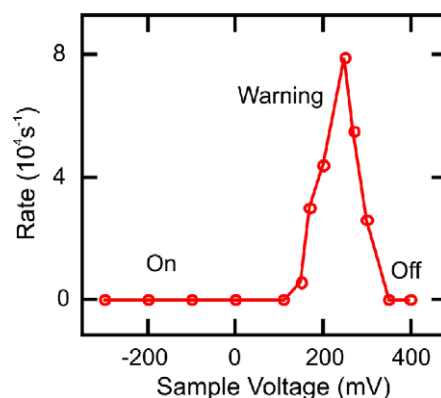


Figure 3. Typical rate of two-level fluctuations of a Ag–SnPc–Ag junction versus sample voltage V . The line serves to guide the eye.

(ii) The STM tip apex structure may change. (iii) The entire SnPc molecule may oscillate vertically between the tip and the surface. (iv) The molecule may oscillate in a lateral direction.

According to previous studies, the energy barrier for inversion of SnPc between its up and down states is ~ 3 eV [16]. At the fairly low bias voltages of the experiments ($V < 400$ mV) this barrier appears to be insurmountable by single-electron processes. Moreover, despite the fluctuations, SnPc was never found in its down state after retracting the tip from a SnPc-up molecule. Finally, while SnPc-up can be controllably switched to SnPc-down at elevated bias voltages [16], the reverse process was not observed, most likely because the coupling of the Sn ion to the metal substrate is significantly stronger in Sn-down. Mechanism (i) can safely be excluded.

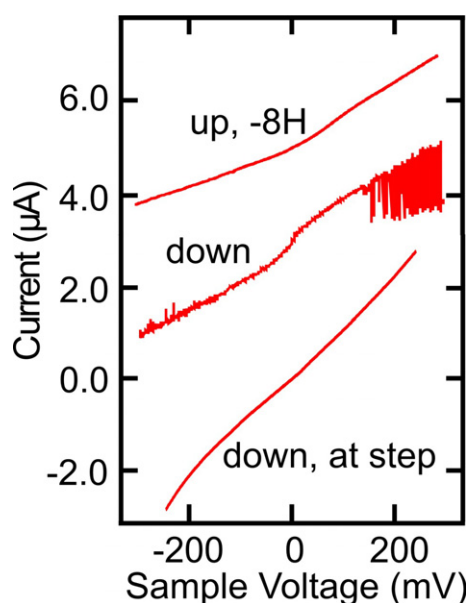


Figure 4. Current–voltage characteristics at contact of SnPc-up on Ag(111) with eight H atoms removed (up, -8H), SnPc-down (down), and SnPc-down at monatomic steps (down, at step). The spectra are shifted vertically by $3\ \mu\text{A}$ and $5\ \mu\text{A}$ for SnPc-down and SnPc-up -8H , respectively.

The relevance of mechanism (ii) was tested by fixing the SnPc molecule more rigidly to the metal surface. This was achieved by removing the eight outermost H atoms of the molecule [15, 17]. The resulting strong chemical bonds between C atoms of SnPc and the Ag substrate are expected to inhibit lateral and vertical motion of the molecule. If current switching still occurred it would be directly related to the status of the tip. However, fluctuations were suppressed at voltages up to 250 mV with $I \sim 2\ \mu\text{A}$ (figure 4, top curve). Thus (ii), tip instability, can be ruled out as a source of the fluctuations observed at $V < 250\ \text{mV}$ with unmodified SnPc.

Regarding mechanism (iii), vertical motion of SnPc, previous contact measurements with CoPc and H_2Pc on Cu(111) may be taken into account [18]. In that work, vertical motion occurred owing to a stronger molecule–tip interaction compared to the molecule–surface interaction. However, it led to transfer of the molecules from the substrate to the tip rather than fluctuations. In the present experiments on Ag(111), removal of SnPc from the surface was not observed. Consequently mechanism (iii) may be discarded. Nevertheless, vertical motion of SnPc deserves some further discussion. In addition to Ag(111), we used Cu(111) and Au(111) as substrates to contact SnPc. From these surfaces, both SnPc-up and -down molecules were picked up by the tips. The case of Ag(111), therefore, is remarkable and implies that a suitable balance of tip–molecule and molecule–surface interactions is present. We further investigated Sn-down molecules on terraces of Ag(111). These contacts do exhibit two-level current fluctuations (figure 4, middle curve). When SnPc molecules are closely packed at monatomic steps of the Ag(111) surface, fluctuations do not occur in the relevant bias range (figure 4, bottom curve).

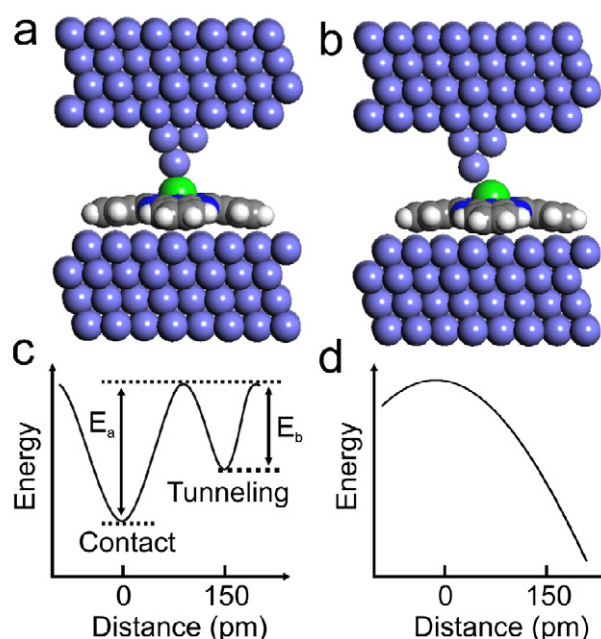


Figure 5. Optimized structures of Ag–SnPc–Ag junctions in the contact ((a), high conductance) and tunnelling ((b), low conductance) states. (c) Schematics of the potential energy of a Ag–SnPc–Ag junction at zero bias as a function of the molecular lateral position on Ag(111). E_a and E_b are diffusion barriers from the tunnelling position to contact and vice versa. (d) Schematic of the electrostatic potential energy induced by the tip at positive sample voltages.

From the experimental data, mechanism (iv), lateral motion of SnPc, remains a possible explanation of the device characteristics [19–21]. To further investigate this process, first principles simulations (SIESTA) and subsequent transport calculations (TRANSIESTA) were performed [22, 23]. The optimized structure of a Ag–SnPc–Ag junction in the low impedance contact state ($I = 1.3\ \mu\text{A}$ at $V = 100\ \text{mV}$) is shown in figure 5(a). In the tunnelling state (figure 5(b)) the SnPc molecule is displaced by $\sim 150\ \text{pm}$. Here, the calculated current is $0.53\ \mu\text{A}$, which is about one third of the contact current. While this reduction is less than experimentally observed (low to high current ratio ~ 0.1), the degree of agreement is acceptable in view of the complexity of the system.

To address the driving force of the switching process, spectra of the differential conductance (dI/dV) of SnPc in the contact regime were recorded. Figure 2(b) shows a stable signal from -300 to $+100\ \text{mV}$ and fluctuations between 100 and 300 mV. The feature centred around 100 mV may tentatively be attributed to the lowest unoccupied molecular orbital (LUMO). At contact, it is shifted down compared to the tunnelling regime, where it is found at $\sim 1\ \text{V}$. Fluctuations commence when the voltage exceeds the LUMO energy, which suggests that the lateral motion of the molecule is due to vibronic excitation involving this orbital. The resonant transfer of electrons to the LUMO leads to a negatively charged and thus transiently reduced molecule. Upon leaving the molecule an electron may deposit energy into vibrational

degrees of freedom and thus induce molecular diffusion below the tip, which leads to fluctuations of the conductance.

We suggest that the particular voltage-dependent switching behaviour is due to the subtle balance between the potential energy of the Ag–SnPc–Ag junction at zero bias (figure 5(c)) and the electrostatic potential introduced by the tip (figure 5(d)). Our DFT calculations show that the potential energy of the contact at zero bias (figure 5(a)) is ≈ 30 meV lower than that of the tunnelling geometry (figure 5(b)). On the other hand, photoelectron spectroscopy data indicate a net charge transfer from Ag(111) to SnPc [24]. The charge distribution of the molecule (along with possible induced moments) interacts with the inhomogeneous electrostatic field at the tip apex. At sufficiently positive sample voltages, i.e. negative tip, the resulting repulsion is expected to favour a lateral displacement of the molecule (figure 5(d)). It also reduces the barrier for lateral hopping from the contact geometry to the tunnelling arrangement. At low or negative sample bias, the contact position below the tip apex is more favourable and the barrier for hopping away from the centre is increased. These energetics are consistent with the observed states of the junction, namely contact at low or negative sample bias, fluctuations at intermediate positive V and tunnelling at $V > +350$ mV. Moreover, the suggested mechanism is reversible upon changing of the bias in agreement with the experimental observations.

In summary, the concept of a molecular safety device based on bias-dependent switching of a Ag–SnPc–Ag junction has been reported. From low voltage to high bias the junction exhibits three states, namely low impedance, two-level fluctuations, and high impedance. These states are interpreted in terms of atomic junction geometries and reversible transitions between them.

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References

- [1] Reed M A, Zhou C, Muller C J, Burgin T P and Tour J M 1997 *Science* **278** 252
- [2] Cui X D, Primak A, Zarate X, Tomfohr J, Sankey O F, Moore A L, Moore T A, Gust D, Harris G and Lindsay S M 2001 *Science* **294** 571
- [3] Smit R H M, Noat Y, Untiedt C, Lang N D, van Hemert M C and van Ruitenbeek J M 2002 *Nature* **419** 906
- [4] Nazin G V, Qiu X H and Ho W 2003 *Science* **302** 77
- [5] Dadosh T, Gordin Y, Krahn R, Khivrich I, Mahalu D, Frydman V, Sperling J, Yacoby A and Bar-Joseph I 2005 *Nature* **436** 677
- [6] Haiss W, Wang C, Grace I, Batsanov A S, Schiffrin D J, Higgs S J, Bryce M R, Lambert C J and Nichols R J 2006 *Nature Mater.* **5** 995
- [7] Repp J, Meyer G, Paavilainen S, Olsson F E and Persson M 2006 *Science* **312** 1196
- [8] Venkataraman L, Klare J E, Nuckolls C, Hybertsen M S and Steigerwald M L 2006 *Nature* **442** 904
- [9] Lortscher E, Weber H B and Riel H 2007 *Phys. Rev. Lett.* **98** 176807
- [10] Solomon G C, Herrmann C, Mujica T H V and Ratner M A 2010 *Nature Chem.* **2** 223
- [11] Galperin M, Ratner M A, Nitzan A and Troisi A 2008 *Science* **319** 1056
- [12] Tao N J 2006 *Nature Nanotechnol.* **1** 173
- [13] Schulze G *et al* 2008 *Phys. Rev. Lett.* **100** 136801
- [14] Wang Y F, Kröger J, Berndt R and Hofer W A 2009 *Angew. Chem. Int. Edn* **48** 1261
- [15] Wang Y F, Kröger J, Berndt R, Vázquez H, Brandbyge M and Paulsson M 2010 *Phys. Rev. Lett.* **104** 176802
- [16] Wang Y F, Kröger J, Berndt R and Hofer W A 2009 *J. Am. Chem. Soc.* **131** 3639
- [17] Zhao A *et al* 2005 *Science* **319** 1542
- [18] Takács A F, Witt F, Schmaus S, Balashov T, Bowen M, Beaurepaire E and Wulfhekel W 2008 *Phys. Rev. B* **78** 233404
- [19] Strosio J and Celotta R 2004 *Science* **306** 242
- [20] Saedi A, van Houselt A, van Gastel R, Poelsema B and Zandvliet H J W 2009 *Nano Lett.* **9** 1733
- [21] Sperl A, Kröger J and Berndt R 2010 *Phys. Rev. B* **81** 035406
- [22] Soler J M, Artacho E, Gale J D, García A, Junquera J, Ordejón P and Sánchez-Portal D 2002 *J. Phys.: Condens. Matter* **14** 2745
- [23] Brandbyge M, Mozos J L, Ordejón P, Taylor J and Stokbro K 2002 *Phys. Rev. B* **65** 165401
- [24] Haeming M, Scheuermann C, Schoell A, Reinert F and Umbach E 2009 *J. Electron Spectrosc. Relat. Phenom.* **174** 59